papers must include the following statement:

# SODIUM BETA BATTERIES

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### INTRODUCTION

Secondary, high-temperature battery technologies that use sodium are attractive candidates for use in many relatively large-scale energy storage applications, including those associated with electric-vehicles (EV), utility generation and distribution, and aerospace. The most promising variants are referred to as sodium beta batteries because of two common and important features: liquid sodium as one reactant and beta"-alumina as the electrolyte. The most well-known of the two primary beta-battery technologies is sodium/sulfur, a system whose promise has motivated continued development for over 25 years. Its characteristics, status, and some general design considerations are included in Sections 1-5. Some 10 years later, the sodium/metal-chloride technology was introduced. Its salient features and development status are described separately in Section 6. Although yet to be marketed, significant advancements have been made with both of these technologies. For example, because of acceptable performance, durability, safety, and manufacturability, automated pilot-production facilities have been or are being built. Production from these plants is permitting precommercialization demonstrations to be conducted.

### 1.0 SODIUM/SULFUR GENERAL CHARACTERISTICS

# 1.1 Advantages/Limitations

A summary of both the attractive properties and the limitations of the sodium/sulfur battery technology is contained in Table 1. These characteristics influence the selection of applications (Section 2) and are utilized or addressed in the design of cells and batteries (Section 5).

### 1.2 Cell Description

Although many hardware designs have been developed, the most advanced use a vertical, cylindrical, monopolar cell. A photograph of four modern cells is shown in Figure 1. Batteries are assembled by configuring cells into series- and parallel-connected arrays to produce the required battery voltage, energy, and power.

Contrary to most electrochemical systems, the reactants and products in a sodium/sulfur cell are always liquid. This approach eliminates the typical morphology-based electrode degradation mechanisms, thus yielding an intrinsically high cycle life. To ensure the active materials remain liquid, each cell must be maintained at a relatively high temperature (300 to 350°C) by encasing the cells collectively in thermal insulation. Electrical heaters are



installed within the enclosures to initially heat the cells and then offset heat loss while the battery is at operating temperature.

TABLE 1.

Advantages and Limitations of the Sodium/Sulfur Battery Technology

CHARACTERISTIC	COMMENT
Advantages	
Potential low cost	Inexpensive raw materials, sealed, no-maintenance configuration
High cycle life	Liquid electrodes
Good energy and power density	Low density active materials, high cell voltage
Flexible operation	Cells functional over wide range of conditions (rate, depth-of-discharge, temperature)
High energy efficiency	100% coulombic efficient, reasonable resistance
Insensitivity to ambient conditions	Sealed, high-temperature systems
State-of-charge identification	Voltage rise and top-of-charge and end-of-discharge
Limitations	·
Thermal management	Effective enclosure to maintain energy efficiency and provide adequate stand time
Safety	Reaction with molten active materials must be controlled
Durable materials	Cell hermeticity is required in a corrosive environment
Freeze/thaw resistance	Weak ceramic electrolyte subjected to stress

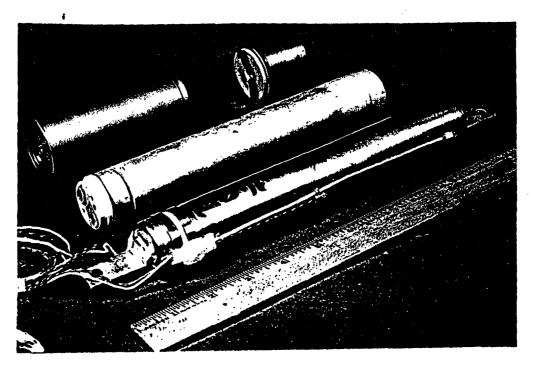


Figure 1. Photographs of Four Sodium/Sulfur cells: SPL-XPB (top left); SPL-PB (top right); ABB-A04 (middle); Ford EVEM (bottom)

A simplified schematic diagram of a modern cell design is shown in Figure 2. Referring to this figure, each cell contains the following components:

Negative (sodium) electrode: This component contains the active sodium that is chemically oxidized during discharge and an inert conductive metal component for transferring current to a terminal (current collector). In Figure 2, the current collector is a combination of the metal rod and the metal container. In most present-day configurations, the sodium is placed on the inside of the electrolyte. This cell configuration is termed central sodium. The metal container is often called the safety can because it effectively limits the quantity of sodium that can be exposed to sulfur in the event of seal or electrolyte failure.

<u>Positive (sulfur) electrode:</u> Constituents include the sulfur that is reduced during discharge and a current collector. In Figure 2, the current collector consists of the external metal container and a layer of compressed carbon or graphite felt within the space between the electrolyte and the container (not shown). The carbon fibers are needed to conduct electrons through the insulating sulfur.

Electrolyte: A solid  $\beta''$ -Al<sub>2</sub>O<sub>3</sub> ceramic functions as the electrolyte by conducting sodium ions (ionic charge transfer) between the positive and negative electrodes. At operating temperature, the conductivity of the  $\beta''$ -Al<sub>2</sub>O<sub>3</sub> is approximately equivalent to that for the electrolytes used in most aqueous batteries. In addition, this component is impermeable to the molten reactants and has negligible electronic conductivity. Thus,

it is also an excellent separator for the molten electrodes, preventing any direct self-discharge and producing 100% coulombic efficiency.

External metal container: This component facilitates packaging and safe handling and, as noted above, functions as a current collector. In a central-sodium cell, the external container must resist corrosive attack by molten sodium polysulfides. The best corrosion-resistant materials identified to date use aluminum or chromium or one of their alloys. Usually chromium-containing layers are coated on an inexpensive substrate.

<u>Seals</u>: To protect cell reactants from external atmosphere, hermetic seals are required. Their design and materials are important because of high temperatures and the presence of internal corrosive liquids. Two types of seals are needed: one to join the  $\beta''$ -Al<sub>2</sub>O<sub>3</sub> electrolyte to an insulating  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> component, and the other to join the metal current collectors to the same  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. The two ceramic components are normally sealed with a glass that is stable in sodium, sulfur, and sodium polysulfides and has a similar coefficient of thermal expansion. The metal-to-ceramic seals use soft metal gaskets and either mechanical or thermocompression bonding.

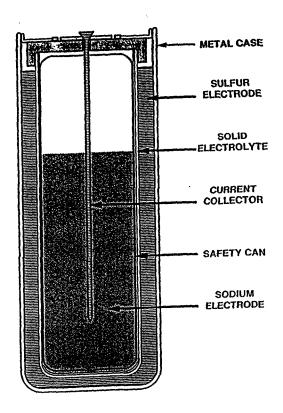


Figure 2. Schematic Diagram of a SPL-XPB Sodium/Sulfur Cell

Battery-level components include mechanical supports for the cells, a thermal management system (incorporating the thermal enclosure), electrical interconnects (cell-cell, cell-bank, bank-battery), possibly cell-failure devices, and safety-related hardware (e.g., thermal fuses).

A comprehensive compilation of the features and characteristics of this technology is contained in the book edited by Sudworth and Tilley, *The Sodium/Sulfur Battery*, Chapman and Hall, 1985 [1].

### 1.3 Cell Electrochemistry and Performance Characteristics

During discharge, the sodium is oxidized at the sodium/ $\beta''$ -Al<sub>2</sub>O<sub>3</sub> interface, forming Na<sup>+</sup> ions. These ions migrate through the electrolyte and combine with the sulfur that is being reduced in the positive electrode compartment to form sodium pentasulfide (Na<sub>2</sub>S<sub>5</sub>). The sodium pentasulfide is immiscible with the remaining sulfur, thus forming a two-phase mixture. After all of the free sulfur phase is consumed, the Na<sub>2</sub>S<sub>5</sub> is progressively converted in a single phase to sodium polysulfides with higher sulfur compositions (Na<sub>2</sub>S<sub>x</sub>, where x = 2.7 to 5). If discharge is continued, another two-phase mixture would again form, except now the second phase would be solid Na<sub>2</sub>S<sub>2</sub>. Cells are normally designed, however, to prevent the formation of Na<sub>2</sub>S<sub>2</sub> because high internal resistance, very poor rechargeability, and potentially structural damage can result. During charge, these simple chemical reactions are reversed. The two half-cell and total cell reactions are as follows:

Negative Electrode: 2Na ₹ 2Na<sup>+</sup> + 2e<sup>-</sup>

charge

Positive Electrode:  $xS + 2e^{-\frac{\pi}{2}} S_x^{\frac{\pi}{2}}$ 

charge

discharge

OVERALL CELL:  $2Na + xS \stackrel{\rightleftharpoons}{=} Na_2S_x$  (x=5 to 2.7),  $E_0 = 2.076 \text{ V}$ 

Although the actual electrical characteristics of the cell are dependent on its design, the general voltage behavior follows that predicted by thermodynamics, as shown in Figure 3. This figure is a plot of the equilibrium potential or open-circuit voltage (OCV) and the working voltages (charge and discharge) as a function of depth of discharge. End-of-discharge is normally defined at OCV values from 1.78 V to 1.9 V. The approximate sodium-polysulfide composition corresponding to 1.9 V/cell is Na<sub>2</sub>S<sub>4</sub> and to 1.78 V/cell is Na<sub>2</sub>S<sub>3</sub>. Many manufacturers have chosen to limit the discharge to less than 100% of theoretical (e.g., to 1.9 V) because of the more corrosive properties of Na<sub>2</sub>S<sub>3</sub> and, due to

nonuniformity of operation throughout the battery, to provide a margin of safety to prevent cells from forming the undesirable solid Na<sub>2</sub>S<sub>2</sub>. In Figure 3, full discharge corresponds to a an end-of-discharge point of 1.9 V.

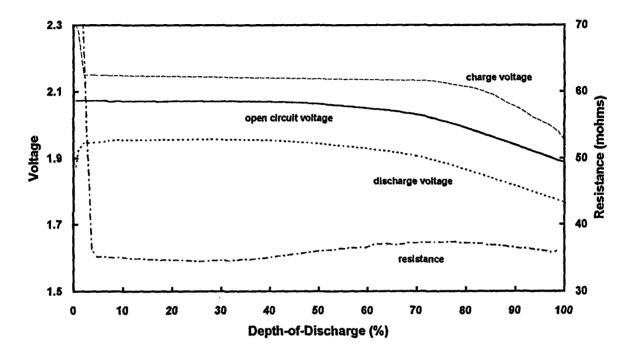


Figure 3. Cell Voltage and Resistance as Function of Depth-of-Discharge (discharge rate = C/3; charge rate = C/5).

Several important characteristics of the sodium/sulfur electrochemical couple are evident from Figure 3. At high states-of-charge, the working voltage during charge increases dramatically due to the insulating nature of pure sulfur (shown also by the high cell resistance). This same factor also causes a slight decrease in cell voltage at the start of discharge. In the two-phase region, the voltages are relatively constant, correlating with an OCV of 2.076 V. Of importance, this characteristic translates into a nearly constant working voltages for 60 to 75% of the discharge, depending on the termination point of the particular cell. Throughout the single phase region, the voltage linearly decreases to the selected end-of-discharge point. At the C/3 discharge rate, the average cell working voltage is approximately 1.9 volts and its theoretical specific energy is 755 Wh/kg (to 1.76 V open circuit). Although not all of the sodium is recovered during the initial charge, cells subsequently deliver 85-90% of their theoretical ampere-hour capacity.

Other important electrical performance characteristics of sodium/sulfur cells are shown in Figures 4 through 8. To ensure consistency, the data presented in these figures were collected at the Sandia National Laboratories using common procedures. The three cells are representative of today's technology and were pictured previously in Figure 1. More information concerning the specific manufacturers of these cells is included in Section 3.2.1, As a note when referring to Section 3, the Powerplex cell is effectively equivalent to the ABB-A04 cell.

The relative insensitivity of the cell voltage-current behavior and peak power to depth-of-discharge ("stiffness") is demonstrated in Figures 4 and 5. A Ragone plot (relation of specific power to specific energy) is shown in Figure 6. When considering the Ragone plot, it is important to remember that these data are for cells. Typically, cells constitute 50-60% of the battery weight. Long-term cycling stability is exhibited by the resistance and capacity response given in Figure 7. Finally, Figure 8 shows that capacity is, in general, not greatly affected by practical discharge or charge rates. However, the capacity of most cells does decline at charge rates greater than C/2.

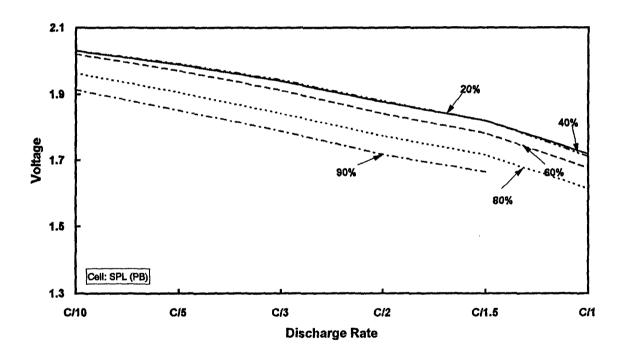


Figure 4. Effect of Discharge Rate on Cell Voltage. Parameter is depth-of-discharge.

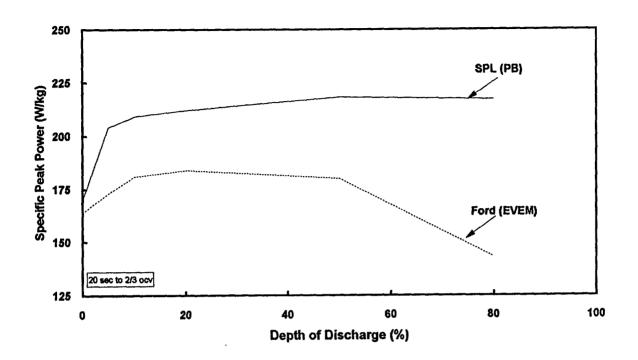


Figure 5.Effect of Depth-of-Discharge on Cell Specific Peak Power.

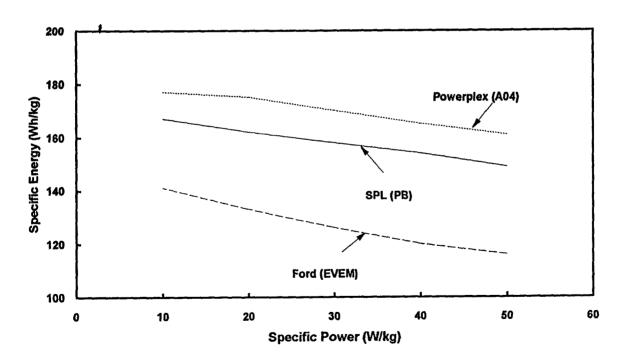


Figure 6. Ragone Plot: Relationship of Cell Specific Power to Cell Specific Energy.

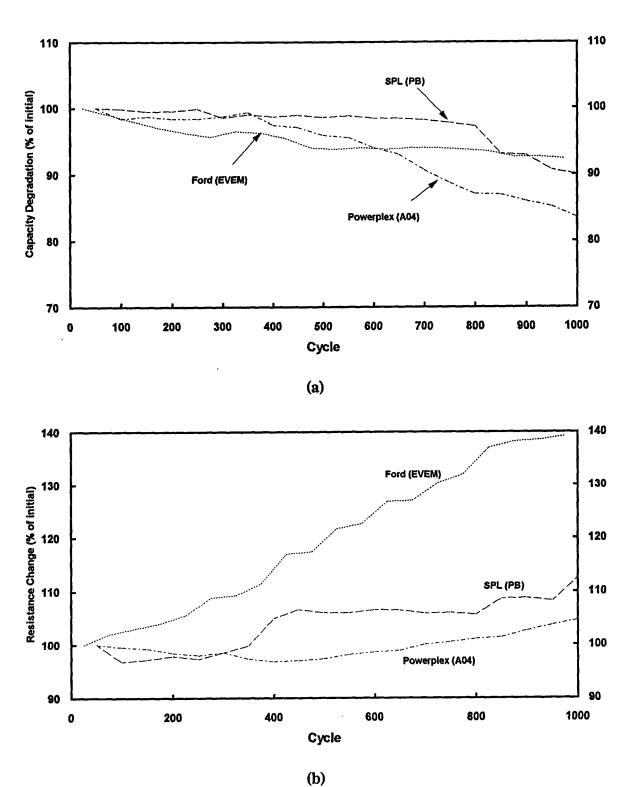
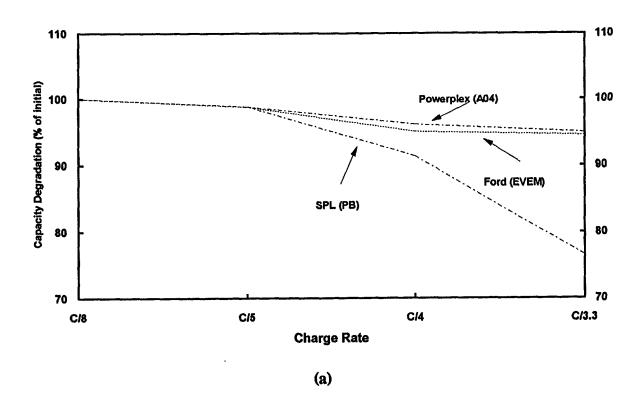
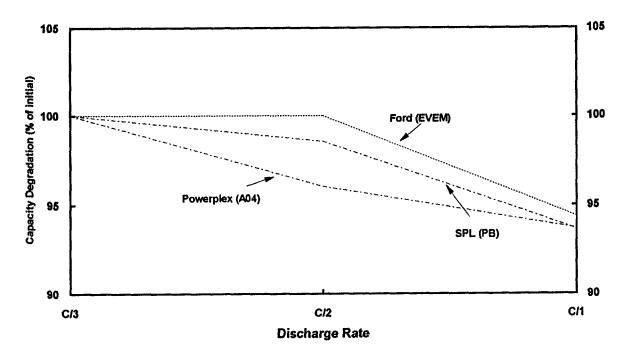


Figure 7. Effect of Cycle Life on (a) Cell Capacity and (b) End-of-Discharge Resistance





(b)
Figure 8.Effect of Charge (a) and Discharge (b) Rate on Cell Capacity Retention.

2.0 APPLICATIONS

When the characteristics of the sodium/sulfur technology are considered, the applications for which a definite benefit exists are those which possess the following critical design criteria:

WEIGHT
OVERALL EFFICIENCY
POWER
CHARGE RATE

ENVELOPE
MAINTAINABILITY
PACKAGING
COST

As an example, the increased energy density and potential for low cost compared with existing battery technologies could favorably impact the following applications:

- <u>electric vehicles</u> for this high volume market to emerge, the range for an electric vehicle (EV) probably must exceed 100 miles and initial cost cannot greatly exceed that for conventionally powered vehicles. For a given physical envelope, sodium/sulfur batteries can provide significantly greater energy (range) at a reduced weight while meeting the vehicle power requirements as compared to existing leadacid or nickel/iron batteries.
- Fork lifts The use of more energetic sodium/sulfur batteries could result in dramatically fewer battery change-outs with associated reduced manpower and capital investment costs.
- <u>Aerospace</u> The lower weight for a given energy and power requirement and cost savings could enable new types of satellite applications to become feasible.

The three principal characteristics that limit the candidate applications include thermal management, cell failure mode, and safety. Thermal considerations are important because of the significant impact thermal management can have on the size, weight, and overall electrical efficiency of the battery. These effects exist because an effective thermal management system must have (a) a very low conductivity insulated enclosure to maintain the battery at its operating temperature, (b) heaters to provide make-up heat during long standby periods, and (c) for certain high power applications, cooling to reject the generated heat. Those applications that are volume/envelope constrained are most impacted. Thermal-related design issues are discussed in greater detail in Section 5.4. In general, consideration of thermal issues leads to the conclusion that sodium/sulfur technology is not attractive from a life-cycle cost perspective for those applications in which:

- a. the operation (charge/discharge cycling) is not relatively continuous. Examples are standby power units, uninterruptible power supplies (UPS), and utility spinning reserve applications that are discharged only several times annually;
- b. the battery is frequently cooled to ambient temperature, allowing the reactants to freeze:
- c. the energy requirement is small (i.e., less than about 5 kWh);
- d. the operation is a continuous, high rate discharge at less than the C/1 rate.

There are exceptions to the above generalizations. These include:

- If inexpensive electrical energy is available for make-up heat, the other attributes of sodium/sulfur may make it viable candidate for some standby and UPS applications.
- The energy requirement limit of less than several kilowatt hours has been shown not to apply for some aerospace applications because size is not a primary design criterion and the high operating temperature is a system benefit because of the ease of heat rejection.
- Specialized sodium/sulfur cells can be designed for high-rate discharge applications, such as defense pulse-power by utilizing ultra-thin sulfur electrodes.

The indeterminacy of the mode of cell failure places a limitation on candidate applications. Cells can fail with a varying high, medium, or low resistance. This characteristic must be considered when cells are networked to satisfy the voltage and capacity requirement of the battery. The two primary networking approaches are the long-series string and the series-parallel array. The former approach requires the use of a device to bypass the cell in the event of its failure. As such, when a cell fails, the battery voltage is reduced by [number of cells in the string]<sup>-1</sup>. The resistance of a failed cell in the latter, series-parallel, networking arrangement will become high, thereby electrically eliminating all cells in that series string. The voltage of the module will not be reduced but its capacity will decrease by that of the failed cell. Therefore, the cell-failure characteristics can affect potential applications because they impose voltage and energy restrictions on the battery. The cell capacity can also play an important role in that the use of smaller cells will allow more parallel strings to be used, thus enhancing reliability for the higher voltage and/or lower energy batteries. Battery networking options are discussed further in Section 5.2.

A third area that must be considered in the selection of potential applications is that of safety. Sodium is a hazardous material because of its reactivity. Developers recognize that redundant features must be incorporated into the cell and battery designs and that safe performance must ultimately be verified experimentally at the battery level for all realistic accident scenarios. Such tests are currently being performed with positive and encouraging

results. However, there may be applications in which the intrinsic reactivity of the constituents may preclude the use of this battery system. For example, the US Navy has been reluctant to consider the sodium/sulfur technology for use in either surface ships or for submarines even though tremendous weight and volume benefits would be gained. The safety of the sodium/sulfur battery is further discussed in Section 5.5.

A preliminary analysis of potential applications suitable for the sodium/sulfur battery was performed based upon the attributes and limitations of the system. The subjective conclusions from this investigation are presented in Table 2. The ratings that are presented in this table are based on a comparison of the sodium/sulfur battery with state-of-the-art batteries currently being used for these applications. Feasibility studies performed for specific applications utilizing "real" requirements could yield different results than those presented in Table 2, especially for those applications with unique requirements. Cost, life, maintenance and economic issues, though justified by analysis, remain to be empirically verified. In general, the information in this table can be used as an application screening tool.

### 3.0 SODIUM/SULFUR BATTERY STATUS

# 3.1 The Developers

Development of the sodium/sulfur technology began in 1966 with the work of Joe Kummer and Neil Weber at Ford Motor Company. A chronology of the sodium beta battery developers is presented in Figure 9. As can be seen, many organizations have been involved throughout this period. The 1980's saw the termination of several significant programs (e.g., Ford, Dow Chemical and General Electric) and the initiation of others. One developer, Beta Research, has turned its development activities away from sodium/sulfur to the sodium/metal chloride system. Those companies currently active in the development and commercialization of the sodium/sulfur technology are listed in Table 3 along with their primary application. The total investment in the development of the sodium/sulfur technology by industry and government is estimated to exceed \$500 million dollars.

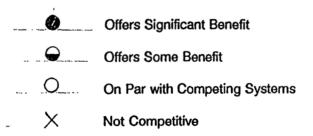
# 3.2 Sodium/Sulfur Cell Development Status

This section focuses on the status of the current sodium/sulfur cell technologies for the electric vehicle (EV) and utility-energy-storage (UES) applications. The majority of the work to date has been directed to these two end-uses and the progress is representative of that achieved for aerospace applications. Furthermore, only the monotube, central sodium configuration shown previously Figure 2 is considered. Other configurations (e.g., glass electrolyte, bipolar flat plate) have been pursued, but with limited success to date. Some of the significant accomplishments of past developers is included for historical reference.

Table 2.

Matching of Applications to Sodium/Sulfur Battery Characteristics

APPLICATION	Weight	Volume	Cost	Life	Maintain- tenance	Safety	Operating Economics
Motive Power			į				
On-Road Vehicles	•	0	<b>(</b>	<b>•</b>	<b>4</b>	0	
Airport Vehicles	- 🐠	<b>9</b>	0	Ф	Φ	0	
Fork Lift Trucks	··· 😝	-	<b>Q</b>	<b>4</b>	0	$\Theta$	
Mining Vehicles	• 🕖	<b>W</b>	0	Ф	0	<b>(</b>	0
Golf Carts	•		×	0	•	0	•
Utility							
Load Levi'g/Peak Sh'vg		•	•	0	<b>(</b>	Ô	0
Dynamic Response	•	•		0	1	Ф	<b>\(\tilde{\to}\)</b>
Spinning Reserve	· 🕣	•	<del>()</del>	$\bigcirc$	$\Theta$	Ф	<b>*</b>
Customer Side of the Mtr	· 🕝	<b>Ø</b>	•	•	•	Ф	•
Standby Power/UPS	0	•	•	0	0	0	×
Defense							
Spacecraft	•	0	<b>4</b>	0	0	0	•
Submarine/Surface Ship		•	<u></u>	<u> </u>		0	<b>(</b>
Tank	0	•	. 🕝	Q -	0	0	<b>O</b>



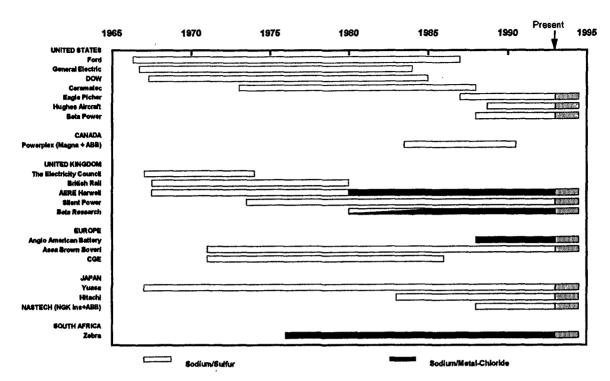


Figure 9. The Developers of the Sodium/Beta Battery

### 3.2.1 Electric Vehicle Cells

The three major developers of sodium/sulfur cells for electric vehicles include Ford Aerospace and Communications Corp. (FACC), Asea Brown Boveri (ABB), and Silent Power Limited (SPL). A photograph of typical cells from each of these organizations was shown previously in Figure 1. A compilation of the physical and performance characteristics of several cells is presented in Table 4. Their performance characteristics were shown in Figures 3-8. Finally, Table 5 contains a summary of many of the design features of the cells from each organization. Further discussion of several of these cells is provided below.

Ford Aerospace: Two generations of EV cell designs were completed and evaluated. The initial design was designated the Electric Vehicle Engineering Model (EVEM) cell that was designed for horizontal operation, a feature that would permit dense cell packing and low-resistance interconnection into modules. The second design was a vertically oriented ETX cell. Approximately 1000 of these cells were eventually built and tested as cells, modules or batteries.

The EVEM cell demonstrated good capacity retention, a low rate of resistance rise, and good peak power density. The longest cell cycle life exceeded 2000 cycles. However, this cell design suffered from an unacceptable infant mortality rate and an inadequate freeze/thaw durability ( $\approx$  3 percent mortality per freeze-thaw cycle). The ETX cell retained many of the critical features of the EVEM cell, but the change to a vertical orientation

provided improved symmetry of stresses associated with freeze-thaw cycling and assured better control of the sodium-feed supply. Other major design changes included: (1) use of an E-Brite stainless steel cell container for improved cycle life, (2) a 33 percent higher capacity, and 3) a flexibly connected sodium reservoir to eliminate possible mechanical stresses on the electrolyte due to misalignment or interference. These cells did demonstrate comparable performance with the EVEM cell as well as improved safety and freeze/ thaw durability [2].

Asea Brown Boyeri: During the 1980's, the A04 cell configuration was the building block of the ABB sodium/sulfur program. Innovations included the use of thermo compression bonding for the electrode seals and aluminum for primary containment. Recently ABB made some subtle, but important, changes to the A04 cell and created their current cell, designated the A08. This cell has retained a nominal capacity of 40 Ah, though discharge is terminated at 1.87 volts open circuit rather than the A04's 1.76 volts. To maintain capacity, the diameter of the A04 was increased by 2 mm. The higher open circuit cut-off voltage significantly decreases the corrosivity of the sodium polysulfide active material allowing the use of lower cost container coatings [3].

Silent Power Limited: A major change in cell design philosophy was adopted in the early 1980's. SPL had been developing a large central-sulfur cell for the EV application since its establishment in 1973. However, problems with freeze/thaw durability, battery reliability (networking considerations), energy density and power forced consideration of dramatically smaller cell designs. A nominal 10-Ah cell, designated the "PB", resulted. This cell has progressed through several major design revisions and remains the basis for the SPL EV batteries.

# 3.2.2 Utility-Energy-Storage Cells

The majority of the development of the sodium/sulfur technology for UES applications has concentrated in Japan and three lead organizations have been involved. To date, load-leveling has been the intended use. Yuasa Corporation has led an effort, as part of the national Moonlight Project, that culminated in the construction and field testing of a 1 MW/8 MWh battery plant. This plant utilized a 300-Ah cell [4,5,6]. Hitachi has been developing several sodium/sulfur cells since 1983 [7,8,9]. Finally, Nastech, a joint venture between ABB and NGK Insulator, is "extending" the ABB EV cell technology for load-leveling uses [10,11]. All three organizations are progressing central sodium monotubular cells with capacities in the range of 150 Ah to 300 Ah. The desire for a cost-effective, high-capacity cell has evolved because of their required, 8-hour, discharge period.

Before the discontinuation of their programs in the mid-80's, two US developers, FACC and General Electric, had also been developing large central sodium cells for the utility load leveling application. The GE cell, designated the FII, had a capacity of 450 Ah; FACC built and tested utility cells having capacities of 150 Ah (Mark-IID), 440 Ah (High Energy), and 1250 Ah (Super Energy). The majority of the FACC effort concentrated on the

Mark-IID cell. Silent Power, in conjunction the US Department of Energy, developed a cell for utility applications that has a nominal capacity of 30 Ah. This cell is essentially an extended version of their EV cell and is designated the XPB cell. This cell remains under development with reliability, freeze-thaw durability and safety improvements being addressed. More than 1000 of these cells have been built, including 200 which were built into a 11 kWh battery. ABB, utilizing its A04 cell, has demonstrated the suitability of its technology for utility-related applications in Germany.

A summary of the physical and performance characteristics of the utility cells from the various developers is presented in Table 6.

Table 3.

Current Sodium/Sulfur Battery Developers and their Principal Intended Application

ELECTRIC VEHICLE	UTILITY ENERGY STORAGE	AEROSPACE
Asea Brown Boveri	Hitachi	Eagle Picher Industries
Silent Power	Nastech	Hughes Aircraft
	Yuasa	

# 4.3 Sodium/Sulfur Battery Development Status

### 4.3.1 Electric-Vehicle Batteries

Requirements imposed by the vehicle on the design of the sodium/sulfur battery are the physical dimensions, voltage, and power, whereas range and weight are normally specified as goals. Key battery design considerations include thermal management, reliability, cell networking, and safety. The approach taken by the two current developers, ABB and SPL, to satisfy these considerations is discussed within Section 5.

The physical and performance characteristics of several ABB and SPL batteries are summarized in Table 7. Photographs of two ABB and two SPL batteries are shown in Figures 10 and 11, respectively. ABB in-vehicle test experience with their first-generation B11 battery has been quite comprehensive [2,12]. B11 batteries have been fitted into the 300 series BMW, the Chrysler Minivan T115, the Daimler Benz 190, a VW Jetta and a VW Caddy. By 1992, ABB battery-powered vehicles have accumulated more than 500,000 km. Results of passenger-car testing include a maximum speed of more than 110 km/hr (64 mph), acceleration to 50 km/hr (31 mph) in 12 seconds at 2/3 battery voltage and a range of 120 km (75 miles). For the Chrysler minivan, the maximum speed was 105 km/hr (65 mph),

acceleration to 50 km/hr took 15 seconds, and the range was up to 75 km (47 miles). Projected range for a specific BMW vehicle currently under development is 350 to 430 km.

Table 4.
Sodium/Sulfur Electric Vehicle Cells:
Their Physical and Performance Characteristics

PARAMETER	CHARACTERISTICS						
Cell Designation	A04	A08	EVEM	ETX	PB (Mk3)		
Developer Capacity, Ah	ABB 38	ABB 40	FACC 41.5	FACC 55	SPL 10.5		
Diameter, mm	35	37.6	36.0	38.0	44		
Length, mm	230	287	252	331	45		
Weight, g	410	417	529	750	120		
Resistance, mΩ	6	8	9.3	7.8	32		
Energy Density, Wh/kg	176	182	145	136	178		
Power Density, W/kg <sup>1</sup>	390	260	215	180	250		
Cycle Life (Weibull) <sup>3</sup> :							
Charac. Life (cycles) Shape Factor	1500 2.0	na² na²	na² na²	na² na²	1871 4.0		

defined at 2/3 open circuit voltage

<sup>&</sup>lt;sup>2</sup> not available

<sup>&</sup>lt;sup>3</sup> cell failure defined as either loss of hermeticity or voltage

Table 5.

Design Features of EV Sodium/Sulfur Cells

DESIGN FEATURE	ABB	FORD	SILENT POWER
Electrolyte	Isostatic Press	Isostatic Press	Electrophoretic Deposition
Sodium Safety Can	yes	yes	yes
Negative Current Collector	safety can	safety can	central "nail"
Sulfur Electrode Structure	carbon felt	carbon felt with low density mat as a resistance barrier	carbon felt with alumina paper as resistance barrier
Container	aluminum constrained within stainless steel can	401SS (EVEM) and E-Brite SS (ETX) with chrome plate	mild carbon steel with duplex chromized coating
Electrode Seals	thermocompression bond	radial compression seal	thermocompression bond

Table 6.
Utility Cell Physical and Performance Characteristics

PARAMETER		FACC	GE		THE ACTIV	SPL
		Mark IID	FII	YUASA	НІТАСНІ	XPB
Cell	diameter, mm	54	63.5	68	75	44
	length, mm	400	998	450	400	114
	weight, g	2000	5880	3600	4000	350
Electrolyte	diameter, mm	34	33	45	50	33
	length, mm	260	568	400	350	100
Sulfur Elect	rode Thick, mm	9.0	12.5	na	na	4.65
Cell Workin	ng Capacity, Ah	150	450	300	280	30
Cell Res	istance, mΩ	10.4	4.1	7.1	na	11.0
Cycle Life (Weibull α/β)		1730/1.37	na	na	na	1330/3.2
Max (	Cycle Life	2300	244	na	1772	1950

<sup>\*</sup> na - not available

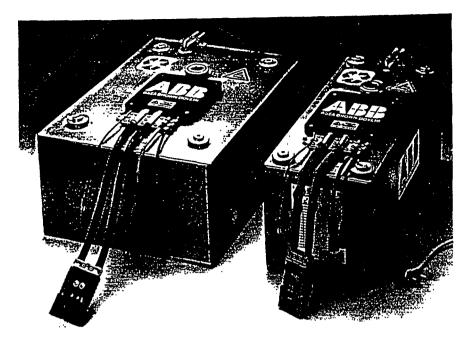


Figure 10. The New Generation of ABB Sodium/Sulfur Batteries: B16 (left) and B17 (right). (Courtesy of Asea Brown Boveri)



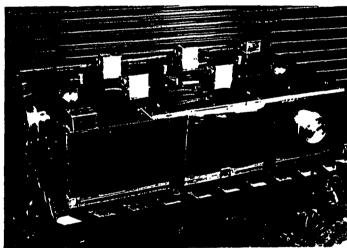


Figure 11. Representative Silent Power Sodium/sulfur Batteries: Bedford (left) and Ford ETX-II (right). (Courtesy of Silent Power, Ltd.)

Table 7.

Physical and Performance Characteristics of Sodium/Sulfur Electric-Vehicle Batteries

PARAMETER	CHARACTERISTICS					
Manufacturer	ABB	ABB	SPL	SPL		
Battery Designation	B11	B17	Bedford	ETX-IIs		
Cell Designation	A04	A08	PB (Mk-3)	PB (Mk-4)		
Energy, kWh	22	19.2	16.8	24		
Dimensions						
Length, mm	1420	730	965	980		
Width, mm	485	540	558	770		
Height, mm	360	315	260	245		
Weight, kg	276	175	210	244		
Voltage, v	90	96	56	100		
Specific Density, Wh/kg	80	118	80	96		
Energy Density, Wh/l1	89	155	120	130		
Specific Power, W/kg	152	na <sup>2</sup>	100	125		
Demonstrated cycles	> 600	na	> 500.	na		

<sup>1</sup> peak power defined at 50% depth of discharge and 2/3 open circuit voltage

Silent Power has built a number of 60-kWh batteries that have been installed in a Bedford CF or Griffon electric vans. The Bedford vans have been operated by Silent Power and by various UK Regional Electricity Boards. A "Bedford" battery was also retrofitted into a Griffon van owned by Electrotek and accumulated more than 13,000 miles. The Griffon achieved a range of 119 miles at a constant maximum speed (52 mph), 163 miles at constant 35 mph speed and 154 miles on the J227aC Schedule. A 50-kWh battery was built for a Ford ETX-II van and was cycled for about 21 months, mainly in the laboratory. The service life of the SPL electric-vehicle battery technology at the beginning of 1992 is approaching two years and 500 to 600 cycles.

Safety at the battery level is being addressed by both developers. ABB reported in

<sup>&</sup>lt;sup>2</sup> not available

1990 about safety tests that were performed in conjunction with the German technical supervising agency "TUV" on their B06 and B11 batteries [13]. These tests encompassed mechanical shock (crash), deformation, external short, and fire exposure. The positive results of this testing allowed ABB to drive NaS battery powered electric vehicles on public streets in Germany without any additional restrictions. Silent Power also conducted a similar set of tests in 1991 and early 1992 on "Bedford" batteries again with positive results.

### 3.3.2 Stationary-Energy-Storage Batteries

Yuasa: Yuasa Corporation (formally Yuasa Battery Company) designed and fabricated the largest sodium/sulfur battery to date, an integrated 1 MW/8 MWh system. The Yuasa development effort was part of a Japanese national research program called the Moonlight project. The battery was subsequently evaluated in a utility load-leveling application. Several batteries preceded the design and build of the full plant. All of the Yuasa batteries used their 300-Ah cell. Evaluation tests were initially performed on 1 kW-class batteries in 1983 with two 12.5 kW batteries were built and tested in 1986. These units produced an AC-to-AC energy efficiency of 77% during 8-hr charge/discharge cycling and had a footprint of over 50 kWh/m². One module exceeded 400 cycles with little degradation in performance. Later, a 50 kW/400 kWh battery, comprised of 16 of the predecessor 12.5 kW modules, was fabricated and housed in a single, air-cooled, thermal enclosure. Performance was similar to that for the smaller battery [15].

The basis for the final 1 MW/8 MWh battery system was provided by the satisfactory performance of the 50 kW/400 kWh battery. NGK Spark Plug Company was responsible for fabricating the electrolyte tubes for the cells and Yuasa Corporation assumed all other responsibilities for the build of the twenty modules that were used in the plant. Kansai Electric Power Company constructed the building to house the system, and Toshiba Corporation developed and installed a 1 MW DC/AC converter. Due to the large number of cells comprising the battery (26,880), the plant was assembled in two, 500 kW/4 MWh phases. The first half battery was commissioned in fourth quarter 1990 and the second half in the second quarter of 1991. A photograph of 10 of the battery modules is shown in Figure 12. The plant is comprised of two of these 10-module strings connected in parallel. The module functions as a basic unit of the plant. Each module is designed to independently keep its cells at an operating temperature of 315°C. The modules can be replaced with a new one when its performance deteriorates. Specifications and the electrical arrangement of this system are listed in Table 8. The efficiency of the AC/DC power conversion system is 96% one way. The rated power of 1000 kW at the AC terminal corresponds to 1040 kW DC when discharging the battery and 960 kW DC when charging. As of mid-1992, the battery has accumulated more than 200 cycles; one of the modules had to be replaced in the interim [5,6].

Nastech: Tokyo Electric Power Company (TEPCO) is working with both Nastech and Hitachi on sodium/sulfur battery projects. Testing of a 10 kW battery developed by Nastech was initiated in March 1990 at TEPCO's Kawasaki Substation. The battery

employed 1320 ABB A04 cells and had a rated energy of 80 kWh at a voltage of 117 volts [9].

Hitachi: Hitachi has built prototype batteries employing their small 28 Ah cell to investigate the dynamic behavior of the utility-energy-storage battery with respect to electrical performance and thermal management. Batteries with nominal energy contents of 9 kWh and 5 kWh have now been tested. More than 900 electrical cycles over a 2½ year period were accumulated on the 9 kWh battery and 550 cycles over 2 years on the 5 kWh battery. Development on a 10 kW/80 kWh battery using approximately 200 of their large 280-Ah cells was initiated in 1990. A vacuum insulation enclosure will be employed along with active air cooling. Gravimetric and volumetric energy densities are 65 Wh/kg and 60 Wh/l, respectively [16].

Silent Power: Utilizing their XPB cell, Silent Power designed and constructed a 200-cell, 8-volt battery that is representative of a segment of a load-levelling battery module. The purpose of this build and test was to gain empirical design information regarding active thermal management, cell interconnection and bus design. Conventional fiber-board insulation was used and an active air cooling system was incorporated to limit temperature excursions during battery discharge. A photograph of this module is shown in Figure 13. The battery was operated for one year and accumulated more than 300 cycles. The Weibull service-life statistics for the cells in this battery were a characteristic life of 2325 cycles with a shape factor of 1.4 [17].

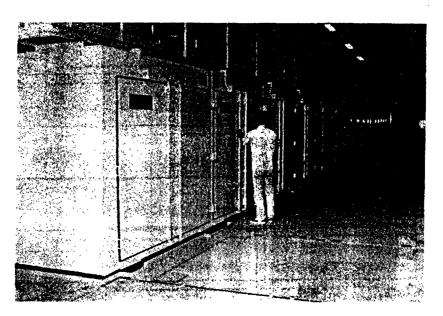


Figure 12. Modules Comprising the 1 MW/8 MWh Moonlight Sodium/Sulfur Battery. (Courtesy of Yuasa Corporation)

Table 8.

Specifications and Electrical Arrangement for the NaS Moonlight Battery Plant

PARAMETER	SPECIFICATION
Location	Tatsumi, Ikuno-ku, Osaka
Output Power	1 MW
Output Capacity	8 MWh
Output Voltage	6600 V AC/1000 V DC
Output Current	1000 amps DC
AC/DC Converter	Self-Commutated Inverter 1200 kVA
Building Area	430 m <sup>2</sup>

LEVEL	ARRANGEMENT
Battery	2 Strings in Parallel 1 MW/8 MWh
String	10 Modules in Series 0.5 MW/4 MWh
Module	14 Sub-Modules in Series 50 kW/400 kWh
Sub-Module	4 Cells in Series with 24, 4-Cell Strings in Parallel

# 4.0 SODIUM/SULFUR FUTURE (PROJECTED CAPABILITY)

Significant progress has been made during the past five years relative to battery-level electrical performance and service life. Still further improvement is possible. For example, performance projections made by the authors for both mid-term (1998) and long-term (2002+) electric-vehicle batteries (listed in Table 10) show that (1) only modest gains are expected in the near future because developers are focusing mainly on completing the manufacturing automation, and (2) that substantial advancement can be made in the future. However, it should be noted that attainment of mid-term performance levels will allow nearly all of the initial requirements of the U.S. automakers to be satisfied. Developers expect that such progress can be made and qualified by 1995. Furthermore, they feel that a cost target

of \$150-200/kWh with a service life of 600 cycles and 5 years is attainable.

The long-term performance projections given in Table 9 are based on a design study recently completed by Beta Power Inc. for the U.S. Department of Energy [18]. This study involved the design of a cell that could be developed using today's cylindrical, monopolar technology, but whose design criteria were driven by actual electric-vehicle specifications. The result is a cell configuration that is expected to be durable, can be efficiently packaged, and possesses an optimum power to energy ratio. Subsequent battery designs confirmed that batteries could be produced that would satisfy the projected requirements of vans and cars into the 21st century. The performance of such batteries could approach the long-term U.S.

auto industry goals.



Figure 13. The SPL 12-kWh Load-Leveling Battery Module. (Courtesy of Silent Power, Ltd.)

Table 9.

Electrical Performance for Sodium/Sulfur Electric Vehicle Batteries

Characteristic	Mid- term goals <sup>1</sup>	Current status <sup>2</sup>	Mid-term capability <sup>3</sup>	Long-term goals <sup>1</sup>	Long-term capability <sup>4</sup>
Energy					
- specific (Wh/kg)	80 (100)	90 - 110	120	200	140
- density (Wh/l)	135	135 - 155	170	300	190
Peak power					
- specific (W/kg)	150 (200)	110 - 130 <sup>5</sup>	140	400	290
- density (W/l)	250	160 - 185 <sup>5</sup>	200	600	400

- Goals defined by the United States Advanced Battery Consortium: mid-term = year 1998 availability; long-term = year 2002 availability. The values are the minimum energy or power at the beginning of life; parenthetical values are desired
- <sup>2</sup> Based on full-size batteries currently available from ABB and SPL
- <sup>3</sup> Uses potential evolutionary improvements with present cell and battery designs
- <sup>4</sup> Battery capability if the new EV cell designed in the Beta Power study [18] for U.S. van applications was available
- 5 Calculated for ABB batteries using reported maximum current and resistance specifications

Relative to the manufacturing aspects of development, both ABB and SPL have progressed manufacturing to the pilot plant level. These plants are currently being used both to engineer production processes and to meet the needs of the vehicle manufacturers for small fleet demonstrations. The first aspect is important because manufacturing techniques applicable to volume production must be validated and opportunities are provided to optimize processing and quality control parameters. These plants are highly automated and employ robotic equipment throughout the process and assembly steps. The ABB pilot plant in Germany has an annual capacity of 10 MWh, corresponding to 500 EV batteries at 20 kWh each [3]. Silent Power has constructed a pilot plant in Northwest England to produce its PB-cell based batteries. Plant capacity is 7.5 MWh storage capacity annually or 375 batteries at 20 kWh each.

### 5.0 SODIUM/SULFUR DESIGN CONSIDERATIONS

Many technical factors exist that must be addressed in the design of sodium/sulfur batteries. Some of the approaches that have been used by manufacturers are briefly described in this section. Design of the cell is presented first and is followed by topics that apply primarily at the battery level: electrical networking, reliability requirements, thermal

management, and safety. Many of the subjects contained in this section are discussed in more detail in Reference 1.

### 5.1 Cell Design Requirements and Variables

Most of the primary cell-design criteria are imposed directly from battery requirements (e.g., energy, power, voltage, service life, weight, and size). These requirements can be termed "battery down." Those key criteria originating at the cell level, termed "cell-up", include cost and manufacturability, safety, and durability. The durability factor is defined as the ability to accommodate mechanical stresses resulting from occasional freeze/thaw cycles or those imposed by vibration and shock. Usually, the battery-down and cell-up requirements conflict forcing compromises to be made. In general, the design engineer must satisfy all requirements by specifying a number of parameters including, among others, cell configuration and geometry, component thickness, and component materials. These influences on the cell design process are shown graphically in Figure 14 and selected parameters are discussed in more detail below.

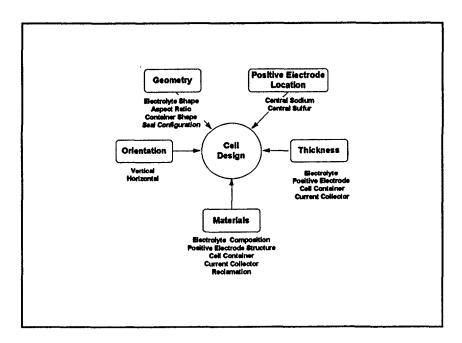


Figure 14. Diagram of Principal Variables to Consider during Cell Design

# 5.1.1 Cell Configuration

<u>Electrolyte Shape:</u> The cell design with a single-electrolyte tube, as discussed in the previous sections, has become the preferred electrolyte configuration primarily because of manufacturing and service-life considerations. Initial attempts to manufacture large-area flat-

plates cells with satisfactory quality have been unsuccessful. Significant problems have been encountered with the seals around the perimeter of the plates because of thermal expansion mismatch and poor chemical durability. Also, the capability of flat-plate cells to accommodate freeze/thaw cycles and vibration has not been validated.

Multi-tube approaches have been proposed as a technique to achieve high power levels, and trial assemblies have been constructed. However, the problems that have precluded serious considerations include difficulty to fabricate the complex alpha-alumina headers, sharing of positive-electrode reactants, overfilling of each tube during recharge, and techniques to prevent self-discharge of the cell after an electrolyte failure.

Aspect Ratio: Several factors influence the practical limits of the aspect ratio (length:diameter) of a cell, including electrolyte manufacturability, cell power:energy ratio, and cell durability. From the perspective of cost and energy density, cells with a large capacity are advantageous. However, the following considerations relative to each of the three aspect-ratio factors force a compromise solution to be sought:

- Longer electrolyte lengths are more difficult to manufacture with acceptable minimum thickness, diameter tolerances and manufacturing yield. Wide tolerances are difficult to accommodate without significant losses in usable cell volume.
- Given other common dimensions, as the electrolyte (and cell) diameter decreases in a tubular configuration, the maximum power density increases. However, a practical limit exists because of deterioration of electrolyte manufacturing yields, gravimetric energy density and cell cost per unit energy. Cell length does not, in general, significantly affect energy density or power, but longer cells cost less per unit of energy. Most cell lengths are limited by an application-related space constraint, by manufacturing-yield considerations, or by the inability to keep the resistance of the current collectors low.
- In standard tubular cell designs, increasing the aspect ratio may have important negative implications on the resistance of the cell to thermal cycling and vibration/shock. These detrimental effects occur because of higher mechanical stresses on the seals and the electrolyte/header interface as the length of the electrolyte increases. Also, nonuniform conditions associated with longer cells can produce reduced safety performance and greater thermal gradients.

Positive/Negative Electrode Location: In the tubular cell design, either sodium or sulfur can be contained within the electrolyte, and the corresponding configurations are referred to as central sodium and central sulfur, respectively. Each configuration has advantages and disadvantages. For example, in the currently preferred central-sodium approach, the cost of a corrosion-resistant cell container is a significant portion of the materials cost. A central-sulfur design would substantially reduce the required quantity of corrosion resistant material and thus provide potential savings. The major disadvantages of

the central sulfur design are is its questionable ability to survive freeze/thaw cycling without damage and its low power (due to a limited current-collector area). Central sodium and central sulfur cells also possess different thermal characteristics because of the relative thermal conductivities of sodium and sulfur. In the central sulfur design, the sodium between the electrolyte and the container provides good heat conduction, whereas in the central sodium design, the sulfur acts as an insulating blanket. Depending on the power requirements of the application, the use of a central-sulfur cell could have a positive effect on thermal management.

Cell Orientation: Cells can theoretically be designed for operation in a horizontal and/or vertical orientation, although success has only been attained with vertical cells. The advantage of a horizontal orientation is greatly improved battery packaging flexibility. For example, the limited height of electric-vehicles batteries eliminates the potential to use long, vertical cells. Additionally, with a horizontal operation, the electrical path length between cells would be minimized, reducing battery resistance and weight. Unfortunately, reactants segregate in horizontal cells due to gravity, producing poor freeze/thaw durability and resistance to vibration and shock. This, coupled with poor sodium distribution, has practically horizontal cells from consideration.

### 5.1.2 Component Thickness

<u>Electrolyte:</u> Currently, the electrolyte contributes a significant portion to the total cell resistance, a factor directly related to its thickness. A thinner electrolyte tube reduces cell resistance, although a penalty on manufacturing yields and mechanical strength is usually incurred.

<u>Positive Electrode:</u> The structure (see Section 5.1.4) and thickness of the positive-electrode can have a substantial effect on cell resistance, polarization (effect of charge and discharge rate), and recharge characteristics. Increasing thickness degrades all three of these performance parameters. The relationship between positive-electrode thickness and performance requires accurate modelling to ensure that the correct projections of performance are made when changing cell dimensions.

<u>Container:</u> The cost and weight of the cell container and the available internal cell volume are related to container wall thickness. Cost is influenced mainly by the fabrication method and the cell aspect ratio. Typically, containers with an aspect ratio of less than 4 can be readily pressed from relatively thin material.

#### 5.1.4 Cell Materials

<u>Positive Electrode</u>: Two different methods have been developed for constructing sulfur electrodes that have good recharge characteristics. The purpose of both is to reduce the amount of elemental sulfur on the electrolyte surface. One method uses physical components that are preferentially wet by sodium polysulfides and the other alters the electrical potential

distribution in the sulfur electrode by using graded porosity carbon or graphite felt. Generally, the first method produces cells with better recharge characteristics, but because the cells have a more complicated structure, this method can be more costly. The primary advantages of the graded felt approach are cost and better lower-temperature operation.

Container: A major materials challenge associated with central-sodium cells is the identification of a suitable sulfur container. The solution to this problem is difficult because the container must be very corrosion resistant, have a surface with reasonable electrical conductivity, possess good mechanical properties, and yet be light weight and inexpensive. Corrosion is detrimental not only because of its direct impact on cell lifetime but also because corrosion products can cause the electrical performance of the cell to degrade. A container constructed with a single material has proven impractical because the two known corrosion resistant, electrically conductive metals (molybdenum and chromium) are generally too expensive and/or difficult to fabricate. Additionally, molybdenum sometimes produces irreversible cell polarization problems. Aluminum has excellent durability in the presence of corrosive sodium polysulfides, but forms a non-conducting sulfide product layer. Although a few nickel-based superalloys and stainless steels have fair resistance to molten sodium polysulfides, their corrosion rate is too high for the very long life desired for these cells (> 5 years). Thus with unacceptable single component containers, manufacturers have been forced to select and use composite materials. These are usually an inexpensive substrate (e.g. aluminum, carbon steel, stainless steel) that has been coated, plated, or sheathed with at least one corrosion-resistant material. The key to success of these composites is to ensure that the corrosion-resistant layer is defect free, thus preventing undermining, substrate attack, and spalling.

Reclamation: Ultimately, all batteries, including sodium/sulfur, will reach their end-of-life and must be reclaimed or disposed in some manner. In addition to sodium and sulfur, sodium polysulfide is classified as a hazardous material because of its corrosivity. Several developers currently use chromium and/or chromium compounds as coatings for containment corrosion protection; these materials are also hazardous because of their toxicity. Therefore, sodium/sulfur batteries used in all terrestrial applications, will have to be returned to a processing center for proper recycling, reclamation, or disposal. This requirement represents an impact on cost, because, at best, the use of low-cost materials of construction will preclude any net value to be attained from a reprocessing operations. Using large-scale commercial plants, a net reclamation cost of <\$5/kWh is believed to be possible given proper attention to materials selection and component construction.

### 5.2 Electrical Networking

During the lifetime of a battery, individual cells will fail that will result in a degradation of electrical performance and life. The rate of degradation is primarily a function of the failure characteristics of the cells and the electrical networking configuration of the battery. Some compensation can be provided with additional capacity at the beginning of life. However, with some battery configurations, especially those with higher voltages

(e.g., 200+ V), the impact of small numbers of cell failures can be significant. The effects of cell failure must therefore be mitigated or controlled in the battery.

Cells must be connected in series to produce the required battery voltage. If the cell capacity is less than the required battery capacity, then further connection of strings in parallel is necessary. Basic options available for configuring cells to produce similar battery output are shown in Figure 15. Each configuration can satisfy the same nominal requirements of voltage and capacity, but each possesses benefits and disadvantages that depend on several cell characteristics, the important ones being the reliability of the cell population, the electrical behavior of the cell during and after failure, and the cell capacity. Because, in general, cell reliability has not been adequately high and the cell failure mode is indeterminate, the choice of battery network can be critical. An indeterminate failure mode refers to a cell resistance that can be high, low, intermediate, and/or variable. In addition, as discussed in the next few paragraphs, the battery configuration can influence safety.

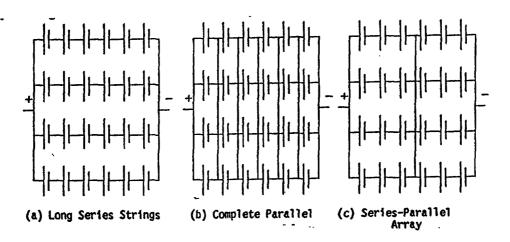


Figure 15. Basic Options for Cell Networking

Long-Series Strings: A cell must fail with a low resistance and be capable of carrying normal operating currents if the long-series string option (Figure 15a) is used. Otherwise, a single cell failure will force the entire string to become inoperative. If this condition cannot be guaranteed, a device is needed in parallel with each cell whose function is triggered by cell failure and then effectively allows current to by-pass the cell. Some proprietary success has been attained with the development of such a device. An important aspect of the failure devices is that their reliability must be high. Otherwise, premature cell shorting is possible. Also, strings with large numbers of cells are not recommended because the first cell to recharge can experience a high over-voltage that is proportional to the number of cells in a string. An even higher over-voltage condition can be produced if a string contains failed cells.

Total Parallel Connection: If the total parallel option (Figure 15b) is used, then the resistance of each failed cell must be high to prevent discharge of the remaining cells in

parallel. Again, because this condition hardly ever exists in practice, a device must be placed in series with each cell that open circuits on cell failure. Such a device must have a very low electrical resistance prior to triggering. To date, no success has been made with the development of such a device.

Series-Parallel Combination: The series-parallel combination (Figure 15c), where parallel connections are provided at frequent intervals along the series string, provides a compromise between the first two options and can eliminate the need for separate and very reliable cell-failure devices. For example, Silent Power Limited (SPL) currently uses a four-cell string sub-unit with parallel interconnection at the ends of the string. A cell failure results in recharge of the remaining cells in the string by the other parallel strings. One of these cells, in turn, becomes high resistance at the top-of-charge, preventing further current flow in the string. In effect, a surviving cell acts as an open circuit device. The major disadvantage of this configuration is that the failure of one cell removes four cells from the battery. Furthermore, if large-capacity cells are used, the number of parallel paths in a battery is small, forcing the battery to become vulnerable to cell failure.

<u>Current Practice</u>: ABB and SPL are presently using similar approaches for networking the cells in the battery. The ABB B11 battery had a "six-string cross-connected" configuration with 5 cells in series by 60 strings in parallel. This approach is basically similar to the "four-cell string" approach that SPL is using. Because the ABB cell capacity is nominally 40 Ah compared to 10 Ah for the SPL PB cell, the ABB battery will have 4 times fewer strings in parallel. It has been known for some time that ABB is developing a failure device (short circuit) to be used in conjunction with a long series string cell networking approach.

### 5.3 Cell Reliability Requirements

Battery developers must ensure that their designs will result in a product that has adequate service life. As mentioned in Section 5.2, the rate of battery degradation is mainly a function of the failure characteristics of the cells and the electrical networking configuration of the battery. The failure characteristics of the cells are influenced by most of the factors discussed in Section 5.1. These characteristics are often quantitatively lumped together into a term called reliability. For a particular design and at any stage of development, a cell will possess specific reliability attributes. The sodium/sulfur developers commonly use the two parameter Weibull statistic to describe the reliability of individual cells. This intrinsic information (generated during cell testing) in combination with a selected cell networking configuration (Section 5.2) and the number of required series and parallel strings can, in turn, be used to estimate battery life.

Battery life increases as the number of cell strings in parallel increases. In this regard, the utility-battery applications are much more accommodating because a large number of cells (and strings) are normally required. Electric-vehicle batteries are more limited, especially with the current trend to higher voltage systems (> 250 V). The Weibull

cell-reliability statistics required to achieve a four-year battery life for two battery designs and two interconnection strategies are presented in Figure 16. In the calculations, assumptions included a cycle rate of 250 cycles per year, a 200-volt electric vehicle battery, and incorporation of a cell bypass/shorting device with each cell in the long-series string networking approach. The Weibull characteristic life is related to average cell life and the shape factor is related to the rate of failure. Higher shape factor values indicate increasing failure rate or lower incidence of early failures. For reference, the Weibull statistics for state-of-the-art cells from Silent Power and ABB were shown in Table 4. The increased reliability of using a large number of cells is shown by comparing the "utility battery" to that for the EV battery with long series strings. As shown, the utility-battery design allows a significantly lower cell reliability unless the shape factor is large (i.e. > 5). The impact of cell interconnect strategies is demonstrated by the two EV battery requirements. The 4-cell string approach requires a more reliable cell than does the long-series string configuration. However, a very reliable cell failure device is needed with the long-string approach.

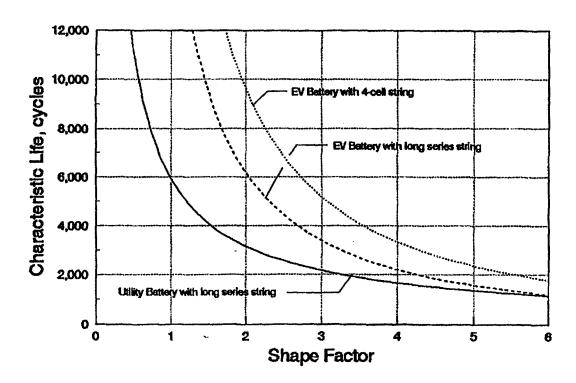


Figure 16. Cell Reliability Requirements to Achieve a Four-Year Battery Life.

### 5.4 Thermal Management

All batteries (e.g., lead-acid, zinc/bromine, etc.) to be used for large-scale energy storage (e.g., utility-based, electric vehicle) will probably need some form of thermal management. This requirement is obvious for the high-temperature sodium/sulfur technology. Because of space and cost constraints, the electric-vehicle applications impose

particularly difficult demands on the hardware used to control the temperature within the battery -- the thermal management system (TMS). The TMS must minimize heat loss from the battery under normal operating conditions and idle periods to maintain the high efficiency of the technology, yet permit sustained high power periods without reaching unacceptably high temperature or creating undesirable temperature differentials within the battery. To satisfy these technical requirements, the TMS in a sodium/sulfur battery usually includes the following components:

- a thermally insulated battery enclosure,
- an active or passive cooling system,
- a method of distributing heat within the battery enclosure, and
- heaters to warm the battery to operating temperature and to maintain it at operating temperature during long idle periods, if necessary.

The amount and type of thermal insulation used in the thermal enclosure (e.g., conventional, evacuated, variable conductance) is dependent on the intended application. Relevant application requirements that must be considered include the physical size of the battery, the power-to-energy ratio, the duty cycle, and the duration of any "idle" periods. For example, utility-energy-storage applications are not as constrained with respect to weight and volume as those associated with electric vehicles. Therefore, utility batteries can probably use conventional insulation materials.

The batteries for electric vehicles currently must use an evacuated insulation technology to minimize thickness and weight. Both ABB and SPL presently use a double walled, evacuated thermal enclosure with either a fiber board, pressed wool or powder insulation. Chemical gettering agents are placed within the enclosure to maintain the needed low vacuum levels. This type of system has been the only design identified to date that adequately minimizes heat loss while providing the necessary load-bearing capability.

The need for a cooling system is determined by the quantity of heat generated during sustained high rate discharge, the thermal capacitance of the battery, and the upper temperature limit of the battery. The techniques that have been used and/or contemplated include direct and indirect heat exchange with air, indirect liquid-based heat exchange, switched heat pipes, thermal shunts, latent-heat-storage, evaporative cooling, and variable-conductance insulation systems. Currently, ABB is utilizing an active cooling scheme in its current family of EV batteries. The cells are mounted on a flat-plate liquid heat exchanger that transfers excess heat to an external oil/air or oil/water heat sink. If the cell and their interconnect resistances are sufficiently low, the temperature rise incurred by the battery can be accommodated by the thermal capacitance of the battery. This is the desired approach for SPL although they recognize that active cooling will be a necessity for most EV batteries.

A design requirement used to identify suitable thermal insulation systems for electric-vehicle batteries has been imposed by U.S. vehicle manufacturers. This specification equates the weekly energy efficiency loss attributable to make-up heating to the self-discharge losses

of other secondary battery systems. The resulting allowable heat loss is approximately 3.2 W thermal/kWh of energy capacity. Satisfaction of this challenging design guideline would also allow sodium/sulfur to be used in standby power applications that are currently dominated with lead-acid batteries.

# 5.5 Battery Safety

The approach being taken to ensure that the cell and battery designs will be safe under both normal and accident conditions focuses on the prevention of electrical short-circuiting and on minimization of exposure to and interaction with the reactive materials. Relative to accidents, the objective of the manufacturers is to engineer safety to a level that ensures that the presence of the sodium/sulfur battery will not contribute to the severity or consequence of the accident. The specific safety factors that are being addressed in various cell and battery designs include the following:

- Selecting proper materials (e.g., low reactivity, high melting point).
- Limiting the availability and flow of sodium to an electrolyte or seal failure site, thus reducing the potential for large thermal excursions (> 100°C) in cells that can cause damaging cell breaching.
- Using components that eliminate the effect of cell failure on adjacent cells.
- Including thermal and electrical fuses to eliminate potential for catastrophic short circuiting. Part of the prevention of electrical shorting involves battery networking, as in Section 5.2.
- Providing protection against the environmental hazards associated with each application. Using an electric vehicle example, these hazards include water splash, shock, and physical intrusion. In the case of the sodium/sulfur technology, the thermal enclosure is effective against many of these factors.
- Performing failure modes analyses to ensure all hazardous scenarios are considered in the design.
- Including functional redundancy to ensure that improbable or overlooked phenomenon do not result in an unwanted consequence.

The cell itself, the battery networking configuration, and the thermal enclosure all have important safety functions. As noted in Section 3, developers are continuing to address many of the aspects of safety specific to the sodium/sulfur system. Although safe operation is not ensured at this time, these activities serve to demonstrate that with sound engineering, the sodium/sulfur battery can be made safe.

# 6.0 Sodium/Metal Chloride Technology

### 6.1 Introduction

As noted in the introduction, the two sodium/beta battery technologies, sodium/sulfur and sodium/metal-chloride, possess many common features. Except for the positive electrode, most of the previous sodium/sulfur cell and battery configuration discussions are applicable to the sodium/metal-chloride system. However, the change to a metal-chloride positive electrode does produce important operational differences that were initially identified in the mid-1970's. It was not until ten years later that significant progress with its development was announced [19, 20, 21]. The motivation for advancing this technology was provided by its positive attributes relative to sodium/sulfur. That is, some researchers believed that the sodium/metal-chloride

technology could provide easier solutions to many of the problems that have confronted the development of sodium/sulfur. These advantages include:

- Higher cell open-circuit voltage 2.35 V and 2.59 V for the FeCl<sub>2</sub> and NiCl<sub>2</sub> chemistries, respectively (2.076 V for sodium/sulfur).
- Wider operating temperature range the sodium/metal-chloride couples can function at temperatures from as low as 220°C to 450°C, whereas sodium/sulfur is limited to a range from 290°C to approximately 390°C. However, the range over which practical power levels and life can be attained is 250°C to 350°C for the nickel-chloride chemistry [22] versus 310°C to 350°C for sodium/sulfur. This nickel-chloride characteristic provides the opportunity to possibly eliminate active battery thermal management.
- Safer products of reaction the exothermic heats of reaction are lower and the vapor pressure of the reactants are less than atmospheric up to a temperature level of 900°C.
- Less metallic component corrosion the chemistry of the positive electrode is less aggressive than molten  $Na_2S_x$ .
- Assembly in the fully discharged state molded discharged electrode can be used.
- Reliable failure mode if the electrolyte fails, sodium will react with the secondary electrolyte to short-circuit the cell.
- Better freeze/thaw durability because of lower temperature change after solidification of the positive electrode and less thermal expansion mismatch, the sodium/metal-chloride system is reported to be less susceptible to thermal cycling.
- Easier reclamation because spent batteries have value (especially for nickel-chloride), reclamation is an economic necessity. Due to the cell configuration, recycling appears to be a straight-forward process.

Its disadvantages or limitations, again relative to the sodium/sulfur technology, include:

• Higher cost - due to the relatively high cost of nickel (even recycled) if the preferred sodium/nickel-chloride couple is used.

- Lower power density because of higher cell resistance, especially near the end-of-discharge.
- Slightly decreased energy density.
- Limited overcharge protection with the potential for evolution of toxic chlorine gas.

### 6.2 Sodium/Metal-Chloride General Characteristics

In contrast to a sodium/sulfur cell, today's sodium/metal-chloride cell contains a secondary electrolyte in the positive electrode (NaAlCl<sub>4</sub>) along with an insoluble and electrochemically active metal-chloride phase. The secondary electrolyte is needed to conduct sodium ions from the primary  $\beta''$ -Al<sub>2</sub>O<sub>3</sub> electrolyte to the solid metal-chloride electrode.

The initial sodium/metal-chloride concept used antimony trichloride in an acidic, aluminum chloride melt [19]. This concept showed promise but did not produce the expected advantages over sodium/sulfur. Later, the present system was developed and solutions identified to several specific problems. His work reduced consideration of candidate materials to those transition metal chlorides that are insoluble in molten NaAlCl<sub>4</sub> [20, 21]. These cells possess a true solid-state positive electrode with a solid-liquid interface. High power densities could be produced if the surface area could be maximized by using sintered finely divided powders in a porous matrix.

Cells utilizing two transition metal chlorides, nickel and iron, have subsequently been developed. The overall cell reactions for both chemistries are:

$$NiCl_2 + 2Na$$
 $\stackrel{\text{discharge}}{\rightleftharpoons}$ 
 $Ni + 2NaCl$ 
 $E_o = 2.58 \text{ V}$ 
 $\stackrel{\text{discharge}}{\rightleftharpoons}$ 
 $E_o = 2.58 \text{ V}$ 

As shown, during discharge the solid metal chloride is converted to the parent metal and sodium chloride crystals. A schematic diagram of a sodium/nickel-chloride cell is shown in Figure 17. In this example, the sodium is located on the outside of the  $\beta''$ -Al<sub>2</sub>O<sub>3</sub> electrolyte (outside sodium). Contained within the electrolyte is the positive electrode. In a fully charged cell, this electrode is a porous metal matrix of iron or nickel partially chlorinated to the metal dichloride. The remaining metal backbone serves as part of the positive-electrode current collector. About 30% of the metal is used in the actual cell reactions. The matrix is impregnated with the NaAlCl<sub>4</sub> molten salt, the liquid sodium ion conductor that permits sodium transport within the positive-electrode chamber. The sodium compartment is less complex than that of the sodium/sulfur cell because safety features are not used. The approach to primary containment for both the outer container and the electrode seals is

similar to that with sodium/sulfur. As discharge proceeds, the chemical reactions occur from the outside of the solid metal particles inward through an ever increasing thickness of reduced metal. This process accounts for the increasing electrical resistance as the cell continues to be discharged.

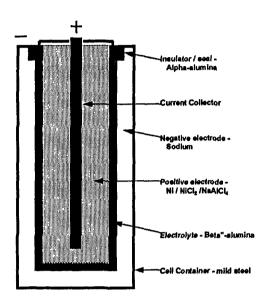


Figure 17. Schematic Diagram of a Sodium/Nickel-Chloride Cell.

The excellent voltage behavior for a sodium/nickel-chloride cell is shown in Figure 18. This figure also includes the thermodynamic potentials for the overall cell reaction and the two cell reactions active during overcharge and overdischarge, respectively. As can be seen, past the end of normal discharge, the working voltage quickly drops. Past this point, all the of the nickel chloride is consumed and the reduction of the NaAlCl<sub>4</sub> to aluminum begins to occur according to the following reaction:

$$3Na + NaAlCl_4 \rightarrow 2NaCl + Al E_o = 1.58 V$$

If continued to the point of complete sodium depletion, electrolyte fracture will occur. But because of the presence of the aluminum, the cell will remain electrically conductive. This characteristic permits batteries to be effectively configured with long series-strings (e.g., Figure 15a). The quick decrease in cell voltage functions as a reliable indicator for the end-of-discharge and is used to provide overdischarge protection. If the cell is overcharged, excess nickel chloride will be produced by the decomposition of the secondary electrolyte

according to the following reaction:

$$2\text{Na} + 2\text{AlCl}_3 + \text{NiCl}_2 \rightarrow \text{Ni} + 2\text{NaAlCl}_4 \qquad E_0 = 3.05 \text{ V}$$

Although degradation of the positive electrode will occur during overcharge, this reaction will prevent voltage-induced fracturing of the  $\beta''$ -Al<sub>2</sub>O<sub>3</sub> electrolyte. In the case of charger malfunction, tests have shown that cells can safely withstand charge voltages 1.5 times higher than normal for at least 12 hours.

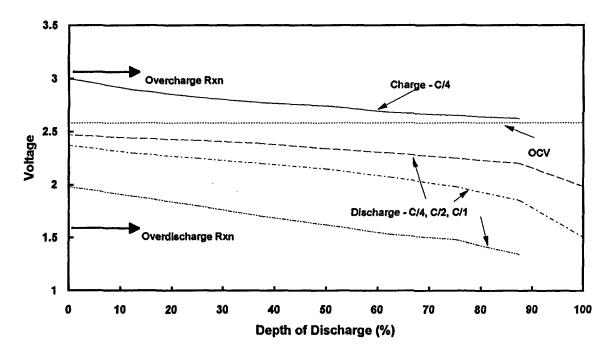


Figure 18. Effect of Depth-of-Discharge on the Voltage of a Sodium/Nickel-Chloride Cell. Arrows indicate overcharge and overdischarge reaction voltages.

Two known deficiencies of the iron-chloride chemistry exist that include (1) an upper temperature limit of  $280^{\circ}$ C where an irreversible eutectic forms that essentially "kills" the cell, and (2) on overcharge, FeCl<sub>3</sub> can be formed which attacks the  $\beta''$ -Al<sub>2</sub>O<sub>3</sub> electrolyte. Due to the high resistance of an iron-chloride cell, especially at the end of discharge, and its high entropy, the  $280^{\circ}$ C temperature limit would probably be routinely exceeded in moderate to high power applications such as electric vehicles. Therefore, even though nickel is more expensive, the nickel-chloride remains the material of choice for the positive electrode.

### 6.3 Sodium/Metal-Chloride Applications

Although some of the specific attributes and limitations are different, the resemblance of general operating characteristics means that the types of applications potentially relevant to

sodium/sulfur are also relevant to the sodium/metal-chloride technology. As such, Table 2 is also qualitatively applicable to the sodium/metal-chloride system. To date, the prime developer of this technology has focused almost exclusively on electric-vehicle applications. Limited attention has been given to utility load-leveling and other low-power applications. Recently, development of sodium/nickel-chloride cells for aerospace applications was undertaken [23]. These cells are essentially EV cells with an optimized positive electrode and wicks for the sodium and the secondary electrolyte to ensure operation in space conditions.

## 6.4 Sodium/Metal-Chloride Development Status

## 6.4.1 The Developers

The effort to develop the sodium/iron-chloride and the sodium/nickel-chloride technologies was initiated in the mid-1970's by Zebra Power Systems. This organization was formed for this purpose by The South African Council for Scientific and Industrial Research (CSIR) and Anglo American Corporation. In the early 1980's, to enhance the development, Zebra Power Systems established a collaborative program with two U.K. organizations, AERE Harwell and Beta Research & Development (Beta R&D). In the late 1980's, a business arrangement was established with a West German company, AEG and the new operating organization founded was named AEG Anglo Battery Holdings (AABH). The principal organizations were included in the sodium/beta technology development chart shown previously in Figure 9, and collectively, AABH is often referred to as the "Zebra" team. AABH now constitutes the only major developer of the sodium/metal-chloride technology. There are also a few, small efforts ongoing outside of this team in the U.S. Some fundamental studies are being performed by Argonne National Laboratories and the Jet Propulsion Laboratory. The Argonne activity is focusing primarily on improving the power characteristics of the positive electrode. Additionally, the U.S. Department of Energy funded a conceptual cell design study at Beta Power, Inc. to evolve designs that could better satisfy future U.S. electric-vehicle requirements.

# 6.4.2 Cell Development Status

As a result of their commonality, the approach taken during the design of the sodium/metal chloride cells has paralleled that used for sodium/sulfur. This conclusion is evident by comparing the two schematic diagrams shown in Figures 2 and 17. The cell designs that have been developed to date are tubular configurations with capacities ranging from 20 Ah to 200 Ah.

The initial work on this technology focused on the iron-chloride chemistry. Later, a discovery was made that the superior properties of nickel chloride could be accessed if cells are fabricated in the discharged state [24]. Work has continued on the iron-chloride variant because of the potential for lower cost and both a central-sodium and outside-sodium configuration have been developed. For the nickel-chloride chemistry, only the outside-sodium

configuration has been developed primarily because a central sodium cell requires the use of a high cost nickel cell container. The first production-oriented cell designs had a relatively high capacity and used a large diameter (55-mm)  $\beta''$ -Al<sub>2</sub>O<sub>3</sub> electrolyte with lengths of 230 mm and 300 mm [25]. The capacity of these cells ranged from 100 to 200 Ah. Prior to using these larger capacity cells in actual batteries, the cell developer, Beta R&D, performed an evaluation to ensure that the cell was safe and could endure actual-use conditions. The safety testing included abuse conditions at the cell level that involved crushing, overcharge, overdischarge, short circuit and over temperature. During the crush test, the typical temperature rise on the outside of a sodium/nickel chloride cell was 100 °C. In the other abuse tests, breaching of the cell case was not observed. The explanations provided for these excellent results are:

- In the event of an electrolyte failure, the sodium reacts with the NaAlCl<sub>4</sub> that is immobilized in the porous structure of the positive electrode. The reaction forms solid products, aluminum and NaCl, around the site of the failure that restrict any further reaction. Furthermore, sodium does not react with the metal or the sodium chloride in the positive electrode.
- The reaction products are relatively noncorrosive.
- All reactants and products have low vapor pressures even at elevated temperatures.
   For example, at 800°C, the vapor pressure for sodium and NaAlCl<sub>4</sub> is less than one atmosphere.

The developers concluded as a result of these tests that it is possible to produce safe, high capacity sodium/metal chloride cells. Because of the good safety performance, the cells could be close-packed into batteries, thus minimizing the degradation of the cell energy density. Collectively, these cells are referred to as "Beta-55" cells. Specifications for two of the cells are listed in Table 10, and batteries were subsequently fabricated with all three cell designs. As can be seen, the developer has not reported the power characteristics of these cells. The design of the Beta-55 cells were not optimum based on either weight or volume and did not achieve their expected resistance values. In a subsequent decision, priority was given to the nickel-chloride chemistry for their primary application, electric vehicles. Though no reasons for this focus on the nickel system have been reported, the probable cause is the deficiencies of the iron system noted at the end of Section 6.2.

The Zebra development team, recognizing that the nickel Beta-55 cell did not have adequate power for the electric-vehicle application, introduced a new sodium/nickel chloride cell design in 1990 [26, 27]. To accomplish the needed improvement in power capability, the ratio of the electrode area to cell capacity was increased. The new cell, called the "Slimline" is based on a 30-mm diameter electrolyte. Its reported characteristics are also listed in Table 10.

Table 10.
Sodium/Metal-Chloride Cell Characteristics

	Cell Configuration				
Characteristic	Beta-55	Beta-55	Slimline		
Positive-Electrode Material	Iron	Nickel	Nickel		
Sodium Location	Internal	Outside	Outside		
Capacity, Ah	200	100	40		
Electrolyte diameter, mm	55	55	30		
Electrolyte length, mm	300	230	230		
Weight, g	2850	2125	800		
Specific Energy, Wh/kg	127	109	124		
Energy Density, Wh/l	194	155	na		
Specific Peak Power, W/kg	na	na	na		
Peak Power Density, W/l	na	na	na		

### 6.4.3 Battery Development Status

Because both sodium/sulfur and sodium/metal-chloride batteries are high temperature systems utilizing cells of comparable voltage and capacity, battery level design issues such as thermal management, cell and module interconnection, component electrical isolation, enclosure design, and enclosure feed-throughs, are similar. As a consequence of this situation and the relatively quick resolution of several cell-level problems, the developers of the sodium/metal chloride technology have already been able to make significant advances. Though the development of the sodium/metal-chloride technology was started approximately ten years after that for sodium/sulfur, it is now at a similar point on its path to commercialization.

The first batteries constructed by the Zebra development team used both the iron-chloride and the nickel-chloride Beta-55 cells [25]. Performance of a 40-kWh battery was evaluated in a vehicle less than one year after the development of the Beta-55 cell had been initiated. The reported physical and performance characteristics for the nickel-chloride and one iron-chloride battery configuration are summarized in Table 11. It should be noted that the iron-chloride values were derived from cell characteristics and a battery design for a utility load-leveling application; and are not based on an actual battery. However, active

liquid cooling was evaluated with an actual electric-vehicle iron-chloride battery, with positive results. As mentioned above, a significant problem with the Beta-55 batteries was their low power capability. This can be seen from the maximum initial power of 11 kW from a 15-kWh nickel-chloride battery.

Initial in-vehicle testing with the Beta-55 batteries were conducted using a converted Suzuki van. This vehicle was equipped with two of the nickel batteries described in the first column of Table 12. The vehicle tare weight was 750 kg. Using 60% of the battery capacity, the range of the vehicle was 115 km at an average speed of 60 km/hr. Top vehicle speed, which was limited by the characteristics of the electric motor, was 71 km/hr.

During the past 4+ years, in-vehicle testing has been conducted with batteries containing the current "Slimline" cell design [22, 26, 27, 28]. The first battery was designed to be consistent with the approximate dimensions of the ABB B11 sodium/sulfur battery. This battery contained 354 cells configured with 59 cells in each series string by 6 strings in parallel; the nominal voltage was 152 volts. The battery was installed in a Mercedes 190, and the vehicle was placed on test in April 1989. During the 7-month evaluation period, the battery accumulated 85 charge/discharge cycles and the vehicle logged 7000 km. At the end of life, three cell failures had occurred due to an accidental overdischarge. To date, eight batteries with the Slimline cell have been built and tested in the Mercedes 190 vehicles. The specifications for the last-reported version is shown in the third column of Table 11. Although these vehicles are relatively heavy (1600 kg), a range of up to 175 km and a maximum speed of 130 km/h have been measured.

A series of safety and abuse tests has been completed in which Zebra batteries have been exposed to overcharge, short circuit, mechanical damage, overheating, vibration, and shock. As reported, "no hazardous effects have been observed and in many cases the battery continued to function" [22]. For example, in a crash test, a hot, charged battery was penetrated with a roadway barrier to a depth equal to 2/3 of its width. Only localized damage occurred and a small quantity of white smoke was emitted, but nothing leaked. Recent testing has also confirmed the excellent freeze/thaw durability of the cells. One particular battery has undergone 30 freeze/thaw cycles without a single cell failure. Cells are routinely exposed to 4 freeze/thaw cycles prior to assembly in batteries.

#### 6.5 Sodium/Metal-Chloride Future

AABH has increased its cell and battery production capability, allowing the in-vehicle evaluations and battery-level safety tests described in Section 6.4 to be performed. By the middle of 1992, over 30,000 nickel-chloride cells had been built and a pilot-production line was under construction. This plant will be capable of producing 10 MWh of batteries by the end of 1993. In addition, a number of design improvements are being made to both the cell and the battery. For example, one advantage of the outside-sodium cell configuration is that an external cell case with a square cross section can be used. This type of cell permits maximum volumetric packing efficiency.

AABH is now projecting that a battery with the specifications listed in the fourth column (Projected) of Table 11 can be produced in the near future. Also, a process to allow the batteries to be recycled is being developed. Of importance, progress has already shown that 90+% of the expensive nickel can be relatively easily recovered in a form potentially suitable for reuse or sale as feedstock to nickel producers.

Concerning service life, AABH solved an early problem with the cell seal and the next life-limiting process has yet to be identified. Cycle life for full-voltage batteries has exceeded 1000 cycles with only a few cell failures, and the service lives for two of the most recent batteries are 900+ and 700+ cycles and one year with no cell failures. In addition, three batteries have been powering vehicles for over a year without any degradation in cells or battery performance [22].

Table 12. Sodium/Metal-Chloride Battery Characteristics

	Battery/Cell Designation					
Characteristic	Beta-55	Beta-55	Slimline	Projected		
Positive-Electrode Material	Nickel	Iron	Nickel	Nickel		
Application	EV	Utility	EV	EV		
Cell Capacity, Ah	100	200	40	na		
Energy, kWh	15	47	30	36		
Power, kW	11	15	34 <sup>*</sup>	47 <sup>*</sup>		
Weight, kg	170	367	306*	277*		
Volume, liters	158	320	265*	211*		
Specific Energy, Wh/kg	88	128	98	130		
Energy Density, Wh/l	95	147	113	170		
Specific Peak Power, W/kg	65	40	109	168		
Peak Power Density, W/l	70	47	131	225		
Demonstrated Life, cycles	na	na	1000	> 1000		

<sup>\*</sup> calculated based on other reported values

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